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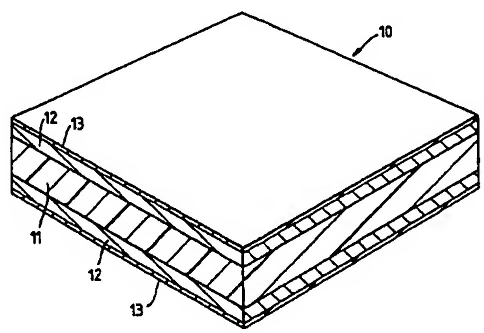
(54) Pyrotechnic sheet material.

(57) The invention provides pyrotechnic sheet material(10) comprising a substrate(11) of oxidizing polymeric film, for example a film of halogenopolymer, having a layer of oxidizable material(12), for example magnesium on at least part of its surface. The substrate and the oxidizable material are capable of reacting together exothermically on ignition. The oxidizable material is covered with an overlying protective barrier layer of passivating material(13) comprising a passive metal or an oxide of a passive metal. The barrier layer is effective to extend the storage life of the pyrotechnic sheet material by providing a dense non-porous oxide layer which prevents oxidization of the oxidizable material until ignition of the pyrotechnic sheet material occurs.



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This invention relates to pyrotechnic material in sheet form and to a method of manufacturing the said material. The material is useful in ignition systems in, for example, gas generators, rocket motors, shock wave transmission tub s, and h at generators of inflators for gas bags of vehicle occupancy safety restraint systems.

Pyrotechnic sheet material consisting of one or more substrate layers of oxidizing polymeric film having a layer of oxidizable material on at least a portion of at least one surface of the, or each, substrate layer, the polymeric film and the oxidizable material being conjointly capable of reacting together exothermically on ignition, has been described in PCT International Publications Nos WO 90/10611 and WO 90/10724. Improved pyrotechnic sheet material having an enhanced burning rate has been described in our co-pending United Kingdom patent application No 9304763.7.

The use of the aforesaid pyrotechnic sheet material to ignite a propellant charge has been described in our co-pending European patent application no 92300835-3 and hybrid inflators containing gas heating elements comprising the pyrotechnic sheet material have been described in our co-pending United Kingdom patent application no 9302503.9.

The preferred oxidizable material of the aforedescribed pyrotechnic sheet material comprises a metal selected from the group consisting of lithium, sodium, magnesium, beryllium, calcium, strontium, barium, zirconium, and alloys comprising any one or more thereof, the most preferred metal being magnesium. Advantageously the metal is vapour-deposited on the film by known methods, the amount of metal being preferably substantially stoichiometric at the location of the film underlying the metal.

We have found that in the aforedescribed pyrotechnic sheet material the layer of oxidizable material oxidizes at a slow but significant rate when stored under normal atmospheric conditions. This effectively progressively diminishes the reaction energy available from the material and would seriously reduce the storage period during which reliable performance could be guaranteed. Thus a layer of magnesium as the oxidizing layer of pyrotechnic sheet material will oxidize at a rate of about 3 microns per year from the surface and if the material were used in a vehicle occupant safety restraint system, where a guaranteed storage life of up to 15 years is required, the thickness of magnesium layer required would be > 60 microns instead of 15-20 microns required for reaction with the oxidizing polymer. We have further found that the oxidizable material can be advantageously passivated by a dense non-porous layer of metal oxide or a metal which has a dense, non-porous xide, thereby significantly incr asing the storage lif of the pyrot chnic sh et material.

In accordance with th pr sent inv ntion a pyrotechnic sheet material comprises a substrate of oxidizing polymeric film; a layer of oxidizable material on at l ast a portion of at least one surface th reof, the substrate and the oxidizable mat rial being conjointly capable of r acting tog ther xothermically on ignition; and a protective barrier layer of passivating material overlying the said oxidizable material, said passivating material comprising a passive metal or an oxide of a passive metal.

In this context a passive metal is a metal on which is readily formed a dense oxide layer that prevents further oxidization of the metal. Examples of suitable passive metals include titanium, aluminium, silicon, chromium, nickel, tin, indium, zinc, copper and alloys comprising any one or more thereof.

Passive metals may be deposited as a layer on the surface of the oxidizable material by vapour deposition at low pressure either by direct evaporation or by magnetron sputtering, the latter being preferred. Oxides of passive metals may be deposited either by direct magnetron sputtering or formed during metal sputtering. Alternatively, metals or oxides may be deposited by magnetron sputtering or from a vapour of a passive metal compound which decomposes or oxidizes to form a passive metal or passive metal oxide. Coating of films by high vacuum vapour-deposition (including magnetron sputtering) are well known in the art of web coating and have been described in the book "Web Processing and Converting Technology" (Van Nostrand Reinhold Company) - chapter entitled "High Vacuum Roll Coating" by Ernst K Harwig. It is generally preferable to deposit a layer of passive metal on the oxidizable material and to allow the passive metal to form a protective dense oxide layer on its surface in storage. Pyrotechnic sheet material having such a protective barrier layer can be stored without significant oxidization of the reactive oxidizable material. The useful life of devices containing the pyrotechnic sheet can thereby be significantly extended.

The deposited layer of passivating material may conveniently and effectively be from 2 to 200 nanometres, preferably 5 to 60 nanometres thick.

Preferably the substrate of oxidizing polymeric film is coated on both sides with oxidizable material but in some cases, for example to facilitate heat sealing of thermoplastic film, portions of the film may be left uncoated.

A particularly preferred oxidizing polymeric film is that used in the pyrotechnic sheet material described in PCT International Publications Nos. WO 90/10611 and WO 90/10724. The oxidizing polymeric film described therein contains atoms chemically bound therein selected from the group consisting of halogens (especially fluorine), oxygen, sulphur, nitrogen and phosph rous. Preferred films comprise fluoropolymer such as polyt traflu roethyl ne (PTFE) but other suitable polym ric films include those comprising polychlorotrifluoroethyl n , polyhexafluoropro-

pylene, copolymers of trifluoroethylene and hexafluoropropylen either with each other or with t trafluoro thylene, copolymers of hexafluoropropyl ne and vinylidene fluoride, copolymers of tetrafluoro- thylene and p rfluoropropyl ne, copolymers of chlorotrifluoroethylene and vinylidene fluoride, homopolymers of perfluoropropylene, copolymers of perfluoropropylene and vinylidene fluoride, trichloroethylene homopolymers, copolymers of trichloroethylene and vinylidene fluoride, mixtures of two or more such polymers or mixtures of any one or more of such polymers with PTFE.

The preferred oxidizable material comprises the aforementioned metals used in the pyrotechnic sheet material described in PCT International Publications Nos WO 90/10611 and WO 90/10724. The preferred metal is magnesium or an alloy thereof. The ratio of metal to the substrate polymer film is preferably substantially stoichiometric at the location of the film underlying the metal. The ignition reaction of a typical pyrotechnic sheet consisting of PTFE and magnesium on ignition can be expressed by the equation

$$2(C2F4)n + 2nMg \rightarrow 2nMgF_2(g) + 2nC_{(s)} + 5.98MJ/kg.$$

The amount of material in the passivating layer will generally be too small to have any significant effect on the reaction and, in particular, it will not give rise to any toxic products which could affect any occupant in a vehicle having a safety restraint system containing the pyrotechnic sheet material.

The rate of energy release on ignition varies inversely with the thickness of the pyrotechnic sheet material and, accordingly, the thickness will be chosen to attain desired energy release. Thus the polymeric film will generally have a thickness of 6 to 60 microns, typically 10-50 microns and the total thickness of the oxidizable metal layer or layers will have the thickness of 2 to 30 microns, typically 10 to 15 microns.

The pyrotechnic sheet material of the invention may be used in any convenient shape or configuration, for example, in flat sheets, strips, tapes or discs, or it may be folded, wrapped, wrinkled, pleated, corrugated, fluted or wrapped around a former such as a rod or tube.

If desired, for enhanced rate and violence of burning, the sheet may be provided with spacer elements, for example protrusions formed on the surface, as described in our co-pending United Kingdom Patent Application No 9304763.7. These spacer elements are effective to prevent intimate contact of adjacent surfaces for example of overlying sheets and thus facilitate rapid combustion of the pyrotechnic material by allowing hot gas and flame to travel ahead of the burning face and initiate the material at d wnstream positions.

The invention also includes a m thod f manufacturing a pyrot chnic sheet material which comprises depositing a layer of oxidizable material on at least a portion of at least on surface of oxidizing polymeric film, the polymeric film and the oxidizabl material being conjointly capable of reacting together exothermically on ignition, and depositing on the oxidizable material an overlying layer of passivating material comprising a passive metal or an oxide of a passive metal.

Preferably the oxidizable material is vapour-deposited at low pressure on a polymer substrate by direct evaporation or magnetron sputtering. The passivating material is preferably vapour-deposited on the oxidizable material by direct evaporation or by magnetron sputtering of a passive metal, or a passive metal compound which decomposes or oxidizes to form a passive metal or passive metal oxide, or by magnetron sputtering of a passive metal oxide.

The invention is further described by way of example only with reference to the accompanying drawing which is a diagrammatic perspective, part-sectional view of the pyrotechnic sheet material of the invention.

Referring to the drawing, pyrotechnic sheet material designated generally by the number 10 consists of a substrate 11 of oxidizing polymeric film, for example of polychlorotrifluoroethylene, coated on each side with a vapour-deposited layer of oxidizable metal for example magnesium 12. Each layer of oxidizable metal is coated with a vapour-deposited layer of passive metal 13.

Embodiments of the invention are further described in the following Examples.

Example 1

A pyrotechnic sheet material was prepared by vapour-depositing a 10 micron thick layer of magnesium evenly on each side of a 20 micron thick substrate of polytetrafluoroethylene (PTFE) film, the total magnesium amouning to 60% of the substrate. Each magnesium layer was then overlaid with a 10 nanometer thick coating of aluminium.

In the preparation of the sheet material magnesium was vapour-deposited onto the substrate polymeric film by direct evaporation at high vacuum and the aluminium was subsequently deposited on the magnesium by magnetron sputtering wherein an ionised stream of Argon gas at low pressure was accelerated onto an aluminium cathode in a magnetic field to eject aluminium atoms or particles at high energy which were deposited on the magnesium surface.

The pyrotechnic sheet material was exposed for 9 weeks in air at 20°C and 90% relative humidity and analysed by electron spectroscopy chemical analysis (ESCA). It was found that hard aluminium oxide had formed to a d pth of 3.6 nan meters below th exposed surface f the aluminium providing a protective layer n the sheet material. In comparison a similar

pyrotechnic sheet material without the aluminium c ating lost almost all its magnesium coating after x-posure for the same period in the same moist atmospheric conditions, the magn sium becoming oxidised and falling away from th substrate.

Example 2

A pyrotechnic sheet material was prepared as described in Example 1 except that the substrate was polychlorotrifluoroethylene and the passive metal coating of aluminium was replaced by a 30 nanometer thick layer of titanium deposited by magnetron sputtering.

Example 3

A pyrotechnic sheet material was prepared as described in Example 1 except that the coating of aluminium was vapour-deposited on the magnesium by direct evaporation at low pressure.

Claims

1. A pyrotechnic sheet material(10) comprising a substrate(11) of oxidizing polymeric film; a layer of oxidizable material(12) on at least a portion of at least one surface thereof, the polymeric film and the oxidizable material being conjointly capable of reacting together exothermically on ignition; characterised by having a protective barrier layer of passivating material overlying the said oxidizing material, said passivating material comprising a passive metal(13) (as defined herein) or an oxide of a passive metal.

2. A pyrotechnic sheet material as claimed in claim 1 characterised in that the layer of passivating material(13) is a vapour-deposited layer.

3. A pyrotechnic sheet material as claimed in claim 1 or claim 2 characterised in that the layer of passivating material(13) is from 2 to 200 nanometres thick.

4. A pyrotechnic sheet material as claimed in any one of claims 1 to 3 characterised in that the substrate(11) of oxidizing polymeric film is coated on both sides with a layer of oxidizable material(12) and each layer of oxidizable material is coated with a layer of passivating material (13).

5. Pyrotechnic sheet material as claimed in any one of claims 1 to 4 characteris d in that the oxidizing polymeric film(11) c mpris s flu ropolymer selected fr m the group consisting of polytetraflu roethylene, polychl rotrifluoroethylene, polyhexafluoropropylene, copolymers of trifluoroethylene and hexafluoropropylene, copolymers of trifluoroethylene and tetrafluoroethylene, copolymers of h xafluoropropylene and tetrafluoro- thylene, copolymers of hexafluoropropylen and vinylidene fluoride, copolymers of tetrafluoroethylene and perfluoropropylene, copolymers of chlorotrifluoroethylene and vinylidene fluoride, homopolymers of perfluoropropylene, copolymers of perfluoropropylene and vinylidene fluoride, trichloroethylene homopolymers, copolymers of trichloroethylene and vinylidene fluoride and mixtures of two or more such polymers; the oxidizable material(12) comprises a metal selected from the group consisting of lithium, sodium, magnesium, beryllium, calcium, strontium, barium, zirconium, and alloys comprising any one or more thereof vapour-deposited on the polymeric film; and the passive metal (13) comprises vapour-deposited metal selected from the group consisting of titanium, aluminium, silicon, chromium, nickel, tin, indium, zinc, copper and alloys comprising of any one or more thereof.

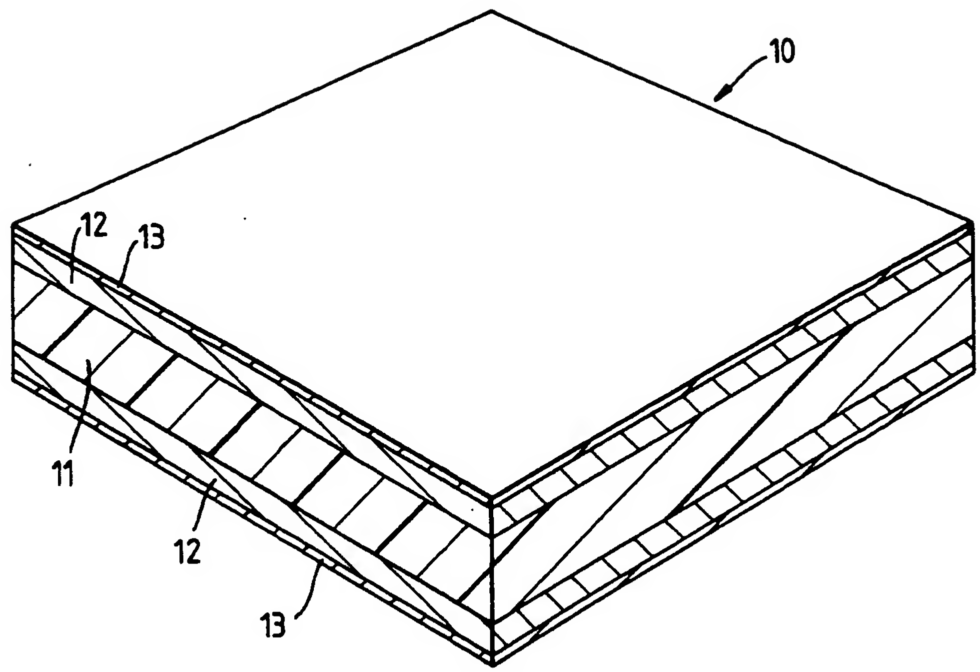
6. Pyrotechnic sheet material as claimed in claim 5 comprising a substrate film(11) of oxidizing polymr 6 to 60 microns thick having vapour-deposited on each side a layer of magnesium(12) 2 to 30 microns thick, characterised by having a vapour-deposited layer of passivating material (13) 5 to 60 nanometers thick overlying the magnesium layer.

7. A method of manufacturing a pyrotechnic sheet material which comprises depositing a layer of oxidizable material(12) on at least a portion of at least one surface of oxidizing polymeric film(11), the polymeric film and the oxidizable material being cojointly capable of reacting together exothermically on ignition, characterised in that an overlying layer of passivating material (13) comprising a passive metal or an oxide of a passive metal is deposited on the oxidizable material.

8. A method as claimed in claim 7 characterised in that the oxidizable material(12) and/or the layer of passivating material(13) are vapour-deposited at low pressure by direct evaporation or magnetron sputtering.

9. A pyrotechnic sheet material whenever prepared by a method as claimed in claim 7 or claim 8.

10. An inflator for a vehicle occupant safety restraint system comprising pyrotechnic sheet material as claim d in any on of the claims 1 to 6 and claim 9.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